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(54) Process for producing ethylene alpha-olefin copolymer.

(57) An ethylene/ α -olefin copolymer of a weight-average molecular weight of not less than 40000 is produced by copolymerization of ethylene with an α -olefin having three or more carbons by use of an olefin polymerization catalyst at a polymerization temperature of not lower than 120 °C, the olefin polymerization catalyst comprising, as constitutional components, a) a metallocene compound, b) an ionizing ionic compound, and c) an organoaluminum compound, the ionizing ionic compound (b) being a compound which is capable of changing the metallocene compound (a) into a cationic form and does not further react with the cationic form of the metallocene compound. This process produces an ethylene/ α -olefin copolymer of high molecular weight in high efficiency.

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The present invention relates to a process for producing an ethylene/ α -olefin copolymer of a high-molecular weight with an olefin polymerization catalyst constituted of a metallocene compound, an organoaluminum compound, and an ionizable ionic compound.

The low-pressure Ziegler process for polymerization of ethylene or an α -olefin is well known in the related technical fields. The catalyst for the process is generally prepared by treating a mixture of an organometallic compound or hydride of a metal of Group 1A to 3A of the Periodic Table with a compound of a transition metal (Group 3B or 2B of the Periodic Table) in a suspension or a solution, or in the absence of a solvent or a diluent.

In recent years, other special kinds of catalysts are being developed which are active in olefin polymerization. Examples of the catalysts are combinations of a cyclopentadienyl derivative of a metal such as titanium, zirconium, and hafnium (Group 4B of Periodic Table) with aluminoxane. (See, for example, J. Boor: "Ziegler-Natta Catalyst and Polymerization", Academic Press, New York (1979), and H. Sinn and W. Kaminsky: Adv. Organomet. Chem. 1899 (1980)). These catalysts have an ability of forming a stereospecific olefin polymer with high catalyst activity.

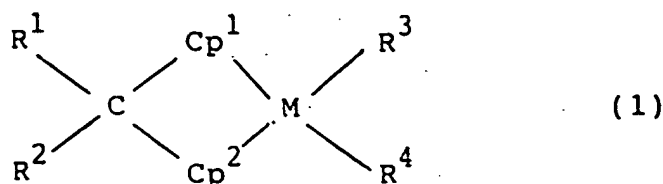
JP-A-1-503788 describes a high-pressure high-temperature process for producing ethylene/ α -olefin copolymer by use of a transition metal compound and an aluminoxane as the catalyst.

Nevertheless, such catalysts have not been used industrially mainly because of the following reasons: the aluminoxane cannot readily be produced in a reproducible form, hindering preparation of the catalyst and the polymer with required reproducibility, and the expensive aluminoxane has to be used in a considerably high ratio to the transition metal compound to achieve sufficient activity.

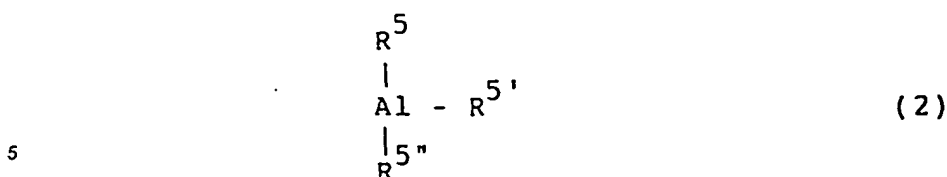
To offset the above disadvantages, JP-A-3-207704 discloses an ionic metallocene compound prepared by reacting a metallocene with an ionizing ionic compound. PCT Application No. WO 92-1723 discloses a process of α -olefin polymerization by use of a catalyst system prepared by reacting a halogenated metallocene with an organometallic compound and then bringing the reaction product into contact with an ionizing ionic compound. This catalyst system is advantageous in olefin polymerization. However, when ethylene and α -olefin are copolymerized by use of such a catalyst system at a high temperature, the resulting copolymer disadvantageously has a low molecular weight. It is the object of the present invention to provide a process for producing an ethylene/ α -olefin copolymer of high molecular weight with high efficiency at a high temperature.

This object could be achieved on the basis of the finding that an ethylene/ α -olefin copolymer having a high molecular weight is obtained with a high catalyst activity by copolymerizing ethylene with an α -olefin by using a specific ionic metallocene catalyst at a temperature of not lower than 120°C.

The present invention provides a process for producing an ethylene/ α -olefin copolymer of a weight-average molecular weight (Mw) of not less than 40000 by copolymerization of ethylene with an α -olefin having three or more carbons by using an olefin polymerization catalyst at a polymerization temperature of not lower than 120°C: the olefin polymerization catalyst comprising, as constitutional components, a) a metallocene compound, b) an ionizing ionic compound, and c) an organoaluminum compound: the metallocene compound (a) being a compound represented by the general formula (1):



wherein Cp¹ and Cp² are independently a substituted or unsubstituted cyclopentadienyl, indenyl, or fluorenyl group; R¹ and R² are independently a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkoxy group, a substituted or unsubstituted aryl group, or a hydrogen atom; M is titanium or zirconium; R³ and R⁴ are independently a hydrogen atom, a halogen atom, a hydrocarbon group of 1 to 12 carbons, an alkoxy group, or an aryloxy group, the ionizing ionic compound (b) being a compound which is capable of changing the metallocene compound (a) into a cationic form and does not further react with the cationic form of the metallocene compound, and the organoaluminum compound (c) being represented by the general formula (2):



wherein R^5 , $R^{5'}$, and $R^{5''}$ are independently a hydrogen atom, a halogen atom, an amino group, an alkyl group, an alkoxy group, or an aryl group, at least one thereof being an alkyl group.

Fig 1 is a 1H -NMR spectrum chart of diphenylmethylene(cyclopentadienyl)(2,7-dimethylfluorenyl)-zirconium dichloride synthesized in

Example 10.

The term "alkyl", whether used alone or as part of another group, e.g. alkoxy, designates residues having preferably 1 to 20, more preferably 1 to 8 and most preferably 1 to 4 carbon atoms. Similarly "aryl" means residues having preferably 5 to 14, more preferably 6 to 12 carbon atoms.

The metallocene compound (a) used in the present invention is represented by the general formula (1).

The metallocene compound is exemplified specifically by

- isopropylidene(cyclopentadienyl)(fluorenyl)titanium dichloride,
- isopropylidene(cyclopentadienyl)(fluorenyl)zirconium dichloride,
- diphenylmethylene(cyclopentadienyl)(fluorenyl)titanium dichloride,
- diphenylmethylene(cyclopentadienyl)(fluorenyl)zirconium dichloride,
- methylphenylmethylene(cyclopentadienyl)(fluorenyl)titanium dichloride,
- methylphenylmethylene(cyclopentadienyl)(fluorenyl)zirconium dichloride,
- isopropylidene(cyclopentadienyl)(2,7-di-t-butylfluorenyl)-titanium dichloride,
- isopropylidene(cyclopentadienyl)(2,7-di-t-butylfluorenyl)-zirconium dichloride,
- diphenylmethylene(cyclopentadienyl)(2,7-di-t-butylfluorenyl)titanium dichloride,
- diphenylmethylene(cyclopentadienyl)(2,7-di-t-butylfluorenyl)zirconium dichloride,
- methylphenylmethylene(cyclopentadienyl)(2,7-di-t-butylfluorenyl)titanium dichloride,
- methylphenylmethylene(cyclopentadienyl)(2,7-di-t-butylfluorenyl)zirconium dichloride,
- isopropylidene(cyclopentadienyl)(2,7-dimethylfluorenyl)-titanium dichloride,
- isopropylidene(cyclopentadienyl)(2,7-dimethylfluorenyl)-zirconium dichloride,
- diphenylmethylene(cyclopentadienyl)(2,7-dimethylfluorenyl)-titanium dichloride,
- diphenylmethylene(cyclopentadienyl)(2,7-dimethylfluorenyl)-zirconium dichloride,
- methylphenylmethylene(cyclopentadienyl)(2,7-dimethylfluorenyl)titanium dichloride,
- methylphenylmethylene(cyclopentadienyl)(2,7-dimethylfluorenyl)zirconium dichloride,
- isopropylidene(cyclopentadienyl)(2,7-diphenylfluorenyl)-titanium dichloride,
- isopropylidene(cyclopentadienyl)(2,7-diphenylfluorenyl)-zirconium dichloride,
- diphenylmethylene(cyclopentadienyl)(2,7-diphenylfluorenyl)-titanium dichloride,
- diphenylmethylene(cyclopentadienyl)(2,7-diphenylfluorenyl)-zirconium dichloride,
- methylphenylmethylene(cyclopentadienyl)(2,7-diphenylfluorenyl)titanium dichloride,
- methylphenylmethylene(cyclopentadienyl)(2,7-diphenylfluorenyl)zirconium dichloride,
- isopropylidene(cyclopentadienyl)(a,i-dibenzofluorenyl)-titanium dichloride,
- isopropylidene(cyclopentadienyl)(a,i-dibenzofluorenyl)-zirconium dichloride,
- diphenylmethylene(cyclopentadienyl)(a,i-dibenzofluorenyl)-titanium dichloride,
- diphenylmethylene(cyclopentadienyl)(a,i-dibenzofluorenyl)-zirconium dichloride,
- methylphenylmethylene(cyclopentadienyl)(a,i-dibenzofluorenyl)titanium dichloride,
- methylphenylmethylene(cyclopentadienyl)(a,i-dibenzofluorenyl)zirconium dichloride,
- isopropylidene(cyclopentadienyl)(b,h-dibenzofluorenyl)-titanium dichloride,
- isopropylidene(cyclopentadienyl)(b,h-dibenzofluorenyl)-zirconium dichloride,
- diphenylmethylene(cyclopentadienyl)(b,h-dibenzofluorenyl)-titanium dichloride,
- diphenylmethylene(cyclopentadienyl)(b,h-dibenzofluorenyl)-zirconium dichloride,
- methylphenylmethylene(cyclopentadienyl)(b,h-dibenzofluorenyl)titanium dichloride,
- methylphenylmethylene(cyclopentadienyl)(b,h-dibenzofluorenyl)zirconium dichloride,
- bis(4-methylphenyl)methylene(cyclopentadienyl)(fluorenyl)-titanium dichloride,
- bis(4-methylphenyl)methylene(cyclopentadienyl)(fluorenyl)-zirconium dichloride,
- bis(4-phenylphenyl)methylene(cyclopentadienyl)(fluorenyl)-titanium dichloride,

bis(4-phenylphenyl)methylene(cyclopentadienyl)(fluorenyl)-zirconium dichloride,
 isopropylidenebis(cyclopentadienyl)titanium dichloride,
 isopropylidenebis(cyclopentadienyl)zirconium dichloride,
 diphenylmethylenebis(cyclopentadienyl)titanium dichloride,
 5 diphenylmethylenebis(cyclopentadienyl)zirconium dichloride,
 methylphenylmethylenebis(cyclopentadienyl)titanium dichloride,
 methylphenylmethylenebis(cyclopentadienyl)zirconium dichloride,
 isopropylidene(cyclopentadienyl)(tetramethyl-cyclopentadienyl)titanium dichloride,
 isopropylidene(cyclopentadienyl)(tetramethyl-cyclopentadienyl)zirconium dichloride,
 10 diphenylmethylene(cyclopentadienyl)(tetramethyl-cyclopentadienyl)titanium dichloride,
 diphenylmethylene(cyclopentadienyl)(tetramethyl-cyclopentadienyl)zirconium dichloride,
 isopropylidenebis(indenyl)titanium dichloride,
 isopropylidenebis(indenyl)zirconium dichloride,
 diphenylmethylenebis(indenyl)titanium dichloride,
 15 diphenylmethylenebis(indenyl)zirconium dichloride,
 methylphenylmethylenebis(indenyl)titanium dichloride and
 methylphenylmethylenebis(indenyl)zirconium dichloride.

For efficient copolymerization, the metallocene compounds are preferred in which the substituent Cp^2 is
 a substituted or unsubstituted fluorenyl group, and/or at least one of the substituents R^1 and R^2 is a
 20 substituted or unsubstituted aryl group.

The ionizing ionic compound (b) used in the present invention is a compound which is capable of
 changing the aforementioned metallocene compound (a) into a cationic form, and does not react further with
 the formed cationic metallocene compound. The ionizing ionic compound is exemplified specifically by
 boron compounds such as

25 tri(n-butyl)ammonium tetrakis(p-tolyl)borate,
 tri(n-butyl)ammonium tetrakis(m-tolyl)borate,
 tri(n-butyl)ammonium tetrakis(2,4-dimethylphenyl)borate,
 tri(n-butyl)ammonium tetrakis(3,5-dimethylphenyl)borate,
 tri(n-butyl)ammonium tetrakis(pentafluorophenyl)borate,
 30 N,N-dimethylanilinium tetrakis(p-tolyl)borate,
 N,N-dimethylanilinium tetrakis(m-tolyl)borate,
 N,N-dimethylanilinium tetrakis(2,4-dimethylphenyl)borate,
 N,N-dimethylanilinium tetrakis(3,5-dimethylphenyl)borate,
 N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate,
 35 triphenylcarbenium tetrakis(p-tolyl)borate,
 triphenylcarbenium tetrakis(m-tolyl)borate,
 triphenylcarbenium tetrakis(2,4-dimethylphenyl)borate,
 triphenylcarbenium tetrakis(3,5-dimethylphenyl)borate,
 triphenylcarbenium tetrakis(pentafluorophenyl)borate,
 40 tropylium tetrakis(p-tolyl)borate,
 tropylium tetrakis(m-tolyl)borate,
 tropylium tetrakis(2,4-dimethylphenyl)borate,
 tropylium tetrakis(3,5-dimethylphenyl)borate,
 tropylium tetrakis(pentafluorophenyl)borate,
 45 lithium tetrakis(pentafluorophenyl)borate,
 lithium tetrakis(phenyl)borate,
 lithium tetrakis(p-tolyl)borate,
 lithium tetrakis(m-tolyl)borate,
 lithium tetrakis(2,4-dimethylphenyl)borate,
 50 lithium tetrakis(3,5-dimethylphenyl)borate,
 lithium tetrafluoroborate,
 sodium tetrakis(pentafluorophenyl)borate,
 sodium tetrakis(phenyl)borate,
 sodium tetrakis(p-tolyl)borate,
 55 sodium tetrakis(m-tolyl)borate,
 sodium tetrakis(2,4-dimethylphenyl)borate,
 sodium tetrakis(3,5-dimethylphenyl)borate,
 sodium tetrafluoroborate,

potassium tetrakis(pentafluorophenyl)borate,
 potassium tetrakis(phenyl)borate,
 potassium tetrakis(p-tolyl)borate,
 potassium tetrakis(m-tolyl)borate,
 5 potassium tetrakis(2,4-dimethylphenyl)borate,
 potassium tetrakis(3,5-dimethylphenyl)borate, and
 potassium tetrafluoroborate;
 aluminum compounds such as
 tri(n-butyl)ammonium tetrakis(p-tolyl)aluminate,
 10 tri(n-butyl)ammonium tetrakis(m-tolyl)aluminate,
 tri(n-butyl)ammonium tetrakis(2,4-dimethylphenyl)aluminate,
 tri(n-butyl)ammonium tetrakis(3,5-dimethylphenyl)aluminate,
 tri(n-butyl)ammonium tetrakis(pentafluorophenyl)aluminate,
 N,N-dimethylanilinium tetrakis(p-tolyl)aluminate,
 15 N,N-dimethylanilinium tetrakis(m-tolyl)aluminate
 N,N-dimethylanilinium tetrakis(2,4-dimethylphenyl)aluminate,
 N,N-dimethylanilinium tetrakis(3,5-dimethylphenyl)aluminate,
 N,N-dimethylanilinium tetrakis(pentafluorophenyl)aluminate,
 triphenylcarbenium tetrakis(p-tolyl)aluminate,
 20 triphenylcarbenium tetrakis(m-tolyl)aluminate,
 triphenylcarbenium tetrakis(2,4-dimethylphenyl)aluminate,
 triphenylcarbenium tetrakis(3,5-dimethylphenyl)aluminate,
 triphenylcarbenium tetrakis(pentafluorophenyl)aluminate,
 tropylium tetrakis(p-tolyl)aluminate,
 25 tropylium tetrakis(m-tolyl)aluminate,
 tropylium tetrakis(2,4-dimethylphenyl)aluminate,
 tropylium tetrakis(3,5-dimethylphenyl)aluminate,
 tropylium tetrakis(pentafluorophenyl)aluminate,
 lithium tetrakis(pentafluorophenyl)aluminate,
 30 lithium tetrakis(phenyl)aluminate,
 lithium tetrakis(p-tolyl)aluminate,
 lithium tetrakis(m-tolyl)aluminate,
 lithium tetrakis(2,4-dimethylphenyl)aluminate,
 lithium tetrakis(3,5-dimethylphenyl)aluminate,
 35 lithium tetrafluoroaluminate,
 sodium tetrakis(pentafluorophenyl)aluminate,
 sodium tetrakis(phenyl)aluminate,
 sodium tetrakis(p-tolyl)aluminate,
 sodium tetrakis(m-tolyl)aluminate,
 40 sodium tetrakis(2,4-dimethylphenyl)aluminate,
 sodium tetrakis(3,5-dimethylphenyl)aluminate,
 sodium tetrafluoroaluminate,
 potassium tetrakis(pentafluorophenyl)aluminate,
 potassium tetrakis(phenyl)aluminate,
 45 potassium tetrakis(p-tolyl)aluminate,
 potassium tetrakis(m-tolyl)aluminate,
 potassium tetrakis(2,4-dimethylphenyl)aluminate,
 potassium tetrakis(3,5-dimethylphenyl)aluminate, and
 potassium tetrafluoroaluminate; but is not limited thereto.

50 The organoaluminum compound (c) used in the present invention is a compound represented by the general formula (2), and exemplified specifically by aluminum compounds such as trimethylaluminum, triethylaluminum, triisopropylaluminum, diisopropylaluminum chloride, isopropylaluminum dichloride, tributylaluminum, triisobutylaluminum, diisobutylaluminum chloride, isobutylaluminum dichloride, tri(t-butyl)aluminum, di(t-butyl)aluminum chloride, t-butylaluminum dichloride, triamylaluminum, diamylaluminum chloride and amylaluminum dichloride, but is not limited thereto.

55 The catalyst may be prepared by mixing the metallocene compound (a), the ionizing ionic compound (b), and the organoaluminum compound (c) mentioned above, for example, in an inert solvent. The method of catalyst preparation is not limited thereto.

The amount of the ionizing ionic compound (b) is preferably in the range of from about 0.1 to 100 moles, more preferably from 0.5 to 30 moles, per mole of the metallocene compound (a).

The amount of the organoaluminum compound (c) is preferably in the range of from 1 to 10000 moles per mole of the metallocene compound (a), but is not limited thereto.

5 The α -olefin of 3 or more carbons used in the present invention includes propylene, 1-butene, 4-methyl-1-pentene, 1-hexene, 1-octene, and styrene, but is not limited thereto. The olefin may be a mixture of two or more thereof.

The process of polymerization includes solution polymerization processes and known high-temperature high-pressure processes.

10 In the solution polymerization, the polymerization temperature is preferably in the range of from 120°C to 300°C, but is not limited thereto provided that the temperature is not lower than 120°C, and the polymerization pressure is preferably in the range of from atmospheric pressure to 200 kg/cm², but is not limited thereto.

15 In the high-pressure polymerization, the polymerization temperature is preferably in the range of from 120°C to 300°C, but is not limited thereto provided that the temperature is not lower than 120°C, and the polymerization pressure is preferably in the range of from 300 to 3500 kg/cm², but is not limited thereto.

By the process described above, an ethylene/ α -olefin copolymer is obtained which has a weight-average molecular weight (Mw) of not less than 40000.

20 The present invention is described below in more detail by reference to Examples without limiting the invention thereto.

The procedures of polymerization, reaction, and solvent purification were conducted in an inert atmosphere. The solvent used in the reaction was purified, dried, and/or deoxidized preliminarily in a conventional method. The compounds used in the reactions were synthesized and identified in conventional methods.

25 The weight-average molecular weight (Mw) of the ethylene/ α -olefin copolymers obtained in Examples were measured by gel permeation chromatography (GPC) employing the apparatus of Model 150C made by Waters Co. with a column of TSK-GEL GMHHR-H(S) (made by Tosoh Corp.) and o-dichlorobenzene as the eluent at a temperature of 140°C at a sample concentration of 7 mg in 10 ml of o-dichlorobenzene.

30 The number of branching of the obtained ethylene/ α -olefin copolymers was measured by FT-IR (Model 5M, made by Nippon Bunko K.K.)

Example 1

35 In a 1-liter reactor, was placed 600 ml of an aliphatic hydrocarbon (IP Solvent 1620, made by Idemitsu Petrochemical Co.) as the solvent. Thereto, 20 ml of hexene was added, and the reactor was kept at a temperature of 150°C. Ethylene was fed to the reactor at an ethylene pressure of 20 kg/cm².

40 Separately, in another vessel, 0.5 μ mol of diphenylmethylene(cyclopentadienyl)(fluorenyl)zirconium dichloride was dissolved in toluene, and thereto a solution of triisobutylaluminum in toluene (triisobutyl aluminum concentration: 20 % by weight) was added in an amount of 125 μ mol in terms of aluminum. The mixture was stirred for one hour. This mixture was added to a solution of 1.0 μ mol of N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate in 1 ml of toluene and the mixture was stirred for 10 minutes. The resulting mixture was introduced into the aforementioned reactor with the aid of nitrogen pressure.

45 After the introduction of the mixture into the reactor, the content in the reactor was stirred at 1500 rpm by keeping the temperature at 150°C for one hour to allow copolymerization to proceed. The obtained reaction product was dried in vacuo at 100°C for 6 hours. Thereby an ethylene/hexene copolymer was obtained in a yield of 25 g. The weight-average molecular weight (Mw) and other measured data are shown in Table 1.

Example 2

50 A copolymer was prepared in the same manner as in Example 1 except for the ethylene pressure of 6 kg/cm². The results are shown in Table 1.

Example 3

55 A copolymer was prepared in the same manner as in Example 1 except that the polymerization was conducted at a temperature of 170°C. The results are shown in Table 1.

Example 4

A copolymer was prepared in the same manner as in Example 1 except that 1.0 μmol of tropylium tetrakis(pentafluorophenyl)borate was used in place of N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate. The results are shown in Table 1.

Example 5

A copolymer was prepared in the same manner as in Example 1 except that 1.0 μmol of triphenylcarbenium (pentafluorophenyl)borate was used in place of N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate. The results are shown in Table 1.

Example 6

A copolymer was prepared in the same manner as in Example 3 except that the hexene was added in an amount of 80 ml. The results are shown in Table 1.

Example 7

A copolymer was prepared in the same manner as in Example 3 except that diphenylmethylene-(cyclopentadienyl)-(fluorenyl)zirconium dichloride, triisobutyl aluminum, and N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate were used respectively in amounts of 0.25 μmol , 62.5 μmol , and 0.5 μmol . The results are shown in Table 1.

Example 8

A copolymer was prepared in the same manner as in Example 7 except that 20 ml of butene was used in place of hexene. The results are shown in Table 1.

Example 9

A copolymer was prepared in the same manner as in Example 8 except that the butene was used in an amount of 70 ml. The results are shown in Table 1.

Example 10

" Synthesis of diphenylmethylene(cyclopentadienyl)(2,7-dimethylfluorenyl)zirconium dichloride "

In 30 ml of THF, was dissolved 3.1 mmol of diphenyl(cyclopentadienyl)(2,7-dimethylfluorenyl)methane. The solution was cooled to -70°C . Thereto 6.8 mmol of n-butyllithium was added dropwise. The mixture was brought to room temperature, and was stirred at room temperature for one day. The THF was removed and the residue was washed with hexane to obtain an orange solid matter.

Separately, in another vessel, 25 ml of methylene chloride was added to 3.1 mmol of zirconium tetrachloride, and the mixture was cooled to -70°C . Thereto a solution of the above orange solid matter in methylene chloride was added, and the mixture was warmed to room temperature. The formed solid matter was removed from the solution by filtration. The filtrate was concentrated and cooled to -70°C . The precipitated crystalline matter was collected from the solution by filtration to obtain 1.0 g of orange-colored crystals of diphenylmethylene(cyclopentadienyl)-(2,7-dimethylfluorenyl)zirconium dichloride. The elemental analysis data and the $^1\text{H-NMR}$ spectrum data are shown below.

Elemental analysis:			
Calculated (% by weight)	C: 67.8%,	H: 4.5%,	Cl: 12.1%
Found (% by weight)	C: 66.5%,	H: 4.8%,	Cl: 11.9%

$^1\text{H-NMR}$ spectrum (CDCl_3): 6.1-8.1 (16H, Flu-H, Ph-H), 5.8 (t, 2H, Cp-H), 6.4 (t, 2H, Cp-H), 2.1 (s, 6H, Me)

Fig. 1 shows the NMR spectrum chart.

" Polymerization "

In a 1-liter reactor, was placed 600 ml of an aliphatic hydrocarbon (IP Solvent 1620, made by Idemitsu Petrochemical Co.) as the solvent. Thereto, 20 ml of hexene was added, and the reactor was kept at a temperature of 170 °C. Ethylene was fed to the reactor at an ethylene pressure of 20 kg/cm².

Separately, in another vessel, 0.25 μmol of diphenylmethylene(cyclopentadienyl)(2,7-dimethylfluorenyl)-zirconium dichloride was dissolved in toluene, and thereto a solution of triisobutylaluminum in toluene (aluminum concentration: 20 % by weight) was added in an amount of 62.5 μmol in terms of aluminum. The mixture was stirred for one hour. This mixture was added to a solution of 0.5 μmol of N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate in 0.5 ml of toluene and the mixture was stirred for 10 minutes. The resulting mixture was introduced into the aforementioned reactor with the aid of nitrogen pressure.

After the introduction of the mixture into the reactor, the content in the reactor was stirred at 1500 rpm by keeping the temperature at 170 °C for one hour to allow copolymerization to proceed. The obtained reaction product was dried in vacuo at 100 °C for 6 hours. Thereby an ethylene/hexene copolymer was obtained in a yield of 34 g. The weight-average molecular weight (Mw) and other measured data are shown in Table 1.

Example 11

" Synthesis of diphenylmethylene(cyclopentadienyl)(2,7-di-t-butylfluorenyl)zirconium dichloride "

In 30 ml of THF, was dissolved 10.6 mmol of diphenyl(cyclopentadienyl)(2,7-di-t-butylfluorenyl)methane. The solution was cooled to -70 °C. Thereto 23.3 mmol of n-butyllithium was added dropwise. The mixture was brought to room temperature, and was stirred at room temperature for one day. Then the THF was removed, and the residue was washed with hexane to obtain an orange solid matter.

Separately, in another vessel, 50 ml of methylene chloride was added to 10.6 mmol of zirconium tetrachloride, and the mixture was cooled to -70 °C. Thereto a solution of the above orange solid matter in methylene chloride was added, and the mixture was warmed to room temperature. The formed solid matter was removed from the solution by filtration. The filtrate was concentrated and was cooled to -70 °C. The precipitated crystalline matter was collected from the solution by filtration to obtain 3.0 g of orange-colored crystals of diphenylmethylene(cyclopentadienyl)(2,7-di-t-butylfluorenyl)zirconium dichloride. The elemental analysis data and the ¹H-NMR spectrum data are shown below.

Elemental analysis:			
Calculated (% by weight)	C: 70.0%,	H: 5.7%,	Cl: 10.6%
Found (% by weight)	C: 69.3%,	H: 6.2%,	Cl: 11.3%

¹H-NMR spectrum (CDCl₃): 6.4-8.1 (16H, Flu-H, Ph-H), 5.8 (t, 2H, Cp-H), 6.4 (t, 2H, Cp-H), 1.2 (s, 18H, tBu)

" Polymerization "

In a 1-liter reactor, was placed 600 ml of an aliphatic hydrocarbon (IP Solvent 1620, made by Idemitsu Petrochemical Co.) as the solvent. Thereto, 20 ml of hexene was added, and the reactor was kept at a temperature of 170 °C. Ethylene was fed to the reactor at an ethylene pressure of 20 kg/cm².

Separately, in another vessel, 0.25 μmol of diphenylmethylene(cyclopentadienyl)(2,7-di-t-butylfluorenyl)-zirconium dichloride was dissolved in toluene, and thereto a solution of triisobutylaluminum in toluene (aluminum concentration: 20 % by weight) was added in an amount of 62.5 μmol in terms of aluminum. The mixture was stirred for one hour. This mixture was added to a solution of 0.5 μmol of N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate in 0.5 ml of toluene and the mixture was stirred for 10 minutes. The resulting mixture was introduced into the aforementioned reactor with the aid of nitrogen pressure.

After the introduction of the mixture into the reactor, the content in the reactor was stirred at 1500 rpm by keeping the temperature at 170 °C for one hour to allow copolymerization to proceed. The obtained reaction product was dried in vacuo at 100 °C for 6 hours. Thereby an ethylene/hexene copolymer was obtained in a yield of 36 g. The weight-average molecular weight (Mw) and other measured data are shown in Table 1.

Comparative Example 1

In a 1-liter reactor, was placed 600 ml of an aliphatic hydrocarbon (IP Solvent 1620, made by Idemitsu Petrochemical Co.) as the solvent. Thereto, 20 ml of hexene was added, and the reactor was kept at a temperature of 150 °C. Ethylene was fed to the reactor at an ethylene pressure of 20 kg/cm².

Separately, in another vessel, 1.0 μmol of ethylenebis(indenyl)zirconium dichloride was dissolved in toluene, and thereto a solution of triisobutylaluminum in toluene (aluminum concentration: 20 % by weight) was added in an amount of 250 μmol in terms of aluminum. The mixture was stirred for one hour. This mixture was added to a solution of 2.0 μmol of N,N-dimethylanilinium tetrakis-(pentafluorophenyl)borate in 1 ml of toluene and the mixture was stirred for 10 minutes. The resulting mixture was introduced into the aforementioned reactor with the aid of nitrogen pressure.

After the introduction of the mixture into the reactor, the content in the reactor was stirred at 1500 rpm by keeping the temperature at 150 °C for one hour to allow copolymerization to proceed. The obtained reaction product was dried in vacuo at 100 °C for 6 hours. Thereby an ethylene/hexene copolymer was obtained in a yield of 40 g. The weight-average molecular weight (Mw) and other measured data are shown in Table 1.

Comparative Example 2

A copolymer was prepared in the same manner as in Comparative Example 1 except that the ethylene pressure was kept at 6 kg/cm².

Comparative Example 3

A copolymer was prepared in the same manner as in Comparative Example 1 except that the polymerization temperature was kept at 170 °.

Comparative Example 4

A copolymer was prepared in the same manner as in Comparative Example 1 except that 1.0 μmol of bis(cyclopentadienyl)zirconium dichloride was used in place of 1.0 μmol of ethylenebis(indenyl)zirconium dichloride. The results are shown in Table 1.

Comparative Example 5

A copolymer was prepared in the same manner as in Comparative Example 1 except that 1.0 μmol of dimethylsilanediylbis(2,4-dimethylcyclopentadienyl)zirconium dichloride was used in place of 1.0 μmol of ethylenebis(indenyl)zirconium dichloride. The results are shown in Table 1.

Example 12

A reactor for high-temperature high-pressure polymerization was employed for the polymerization. Ethylene and hexene were fed continuously with pressure to the reactor to keep the total pressure at 950 kg/cm² and the concentration of hexene at 31.4 mol%, and the reactor was stirred at 1500 rpm.

Separately, in another vessel, a solution of triisobutylaluminum in toluene was added to a solution of diphenylmethylenecyclopentadienyl(fluorenyl)zirconium dichloride in toluene at an aluminum-to-zirconium mole ratio of 250:1. Further thereto, a solution of N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate in toluene was added at a boron-to-zirconium mole ratio of 2:1 to prepare the catalyst solution.

The resulting catalyst solution was continuously introduced into the reactor to allow the polymerization to proceed at the reactor temperature of 193 °C. The results are shown in Table 2 and Table 3.

Example 13

The polymerization was conducted in the same manner as in Example 12 except that the polymerization temperature was controlled to be at 180 °C and the hexene concentration was adjusted to 28.8 mol%. The results are shown in Table 2 and Table 3.

Example 14

The polymerization was conducted in the same manner as in Example 12 except that the polymerization temperature was controlled to be at 165°C and the hexene concentration was adjusted to 19.0 mol%.

5 The results are shown in Table 2 and Table 3.

Example 15

10 The polymerization was conducted in the same manner as in Example 13 except that tropylium tetrakis(pentafluorophenyl)borate was used in place of N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate, and the hexene concentration was adjusted to 32.6 mol%. The results are shown in Table 2 and Table 3.

Example 16

15 The polymerization was conducted in the same manner as in Example 15 except that the polymerization temperature was controlled to be at 165°C and the hexene concentration was adjusted to 33.0 mol%. The results are shown in Table 2 and Table 3.

Example 17

20 The polymerization was conducted in the same manner as in Example 14 except that triethylaluminum was used in place of triisobutylaluminum and the hexene concentration was adjusted to 33.5 mol%. The results are shown in Table 2 and Table 3.

25 Example 18

A reactor for high-temperature high-pressure polymerization was employed for the polymerization. Ethylene and hexene were fed continuously with pressure to the reactor to keep the total pressure at 1500 kg/cm² and the concentration of hexene at 41.2 mol%, and the reactor was stirred at 1500 rpm.

30 Separately, in another vessel, a solution of triisobutylaluminum in toluene was added to a solution of diphenylmethylene(cyclopentadienyl)(fluorenyl)zirconium dichloride in toluene at an aluminum-to-zirconium mole ratio of 250:1. Further thereto, a solution of N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate in toluene was added at a boron-to-zirconium mole ratio of 1:1 to prepare the catalyst solution.

35 The resulting catalyst solution was introduced into the reactor to allow the polymerization to proceed continuously at the reactor temperature of 155°C. The results are shown in Table 2 and Table 3.

Example 19

40 The copolymerization was conducted in the same manner as in Example 18 except that the polymerization temperature was controlled to 180°C, butene was used in place of hexene at a concentration of 39.4 mol%, and the pressure was controlled to 900 kg/cm². The results are shown in Table 2 and Table 3.

Example 20

45 The copolymerization was conducted in the same manner as in Example 19 except that the polymerization temperature was controlled to 153°C, the butene concentration was adjusted to 53.9 mol%. The results are shown in Table 2 and Table 3.

Example 21

50 The copolymerization was conducted in the same manner as in Example 19 except that diphenylmethylene(cyclopentadienyl)(2,7-di-t-butylfluorenyl)zirconium dichloride was used in place of diphenylmethylene(cyclopentadienyl)(fluorenyl)zirconium dichloride, the polymerization temperature was controlled to 150°C, and butene concentration was adjusted to 66.8 mol%. The results are shown in Table 2 and Table 3.

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Example 22

5 The copolymerization was conducted in the same manner as in Example 19 except that diphenylmethylene(cyclopentadienyl)(2,7-dimethylfluorenyl)zirconium dichloride was used in place of diphenylmethylene(cyclopentadienyl)(fluorenyl)zirconium dichloride, the polymerization temperature was controlled to 155 °C, and hexene was used in place of butene at a concentration of 30.0 mol%. The results are shown in Table 2 and Table 3.

Comparative Example 6

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The copolymerization was conducted in the same manner as in Example 12 except that ethylenebis-(indenyl)zirconium dichloride was used in place of diphenylmethylene(cyclopentadienyl)(fluorenyl)zirconium dichloride, the polymerization temperature was controlled to 155 °C, and the hexene concentration was adjusted to 32.0 mol%. The results are shown in Table 2 and Table 3.

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The copolymerization of ethylene with α -olefin with a specified metallocene catalyst at a polymerization temperature of not lower than 120 °C enables production of a copolymer with high catalyst activity with high efficiency.

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Table 1

Example	Metal- locene	Boron compound	Temper- ature (°C)	-Olefin (ml)	Ethylene pressure (kg/cm ²)	Yield (g)	Mw	Mw/Mn	Melting point (°C)	Number of branching (per 1000C)
1	Zr-1	B-1	150	Hexene-1	20	25	75700	2.0	115	7.4
2	Zr-1	B-1	150	Hexene-1	20	16	54700	1.9	104	21.7
3	Zr-1	B-1	170	Hexene-1	20	11	56300	1.9	119	7.0
4	Zr-1	B-2	150	Hexene-1	20	37	73500	1.9	115	7.3
5	Zr-1	B-3	150	Hexene-1	20	12	77000	1.9	115	7.5
6	Zr-1	B-1	170	Hexene-1	80	36	56300	1.9	100	
7	Zr-1	B-1	170	Hexene-1	20	30	49000	2.0	120	
8	Zr-1	B-1	170	Butene-1	20	38	51200	1.8	122	
9	Zr-1	B-1	170	Butene-1	70	22	48400	1.6	93	
10	Zr-2	B-1	170	Hexene-1	20	34	66100	1.8	120	
11	Zr-3	B-1	170	Hexene-1	20	36	67500	1.7	120	
Comparative Example										
1	Zr-4	B-1	150	Hexene-1	20	40	20400	2.2	124	5.9
2	Zr-4	B-1	150	Hexene-1	20	26	15400	2.2	112	10.5
3	Zr-4	B-1	170	Hexene-1	20	28	16500	2.0	124	6.3
4	Zr-5	B-1	150	Hexene-1	20	24	14200	1.9	126	5.2
5	Zr-6	B-1	150	Hexene-1	20	21	23500	2.0	124	5.4

Zr-1: $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$
 Zr-3: $\text{Ph}_2\text{C}(\text{Cp})(2,7\text{-di-tBu-Flu})\text{ZrCl}_2$
 Zr-5: Cp_2ZrCl_2
 B-1: $\text{Ph}(\text{Me})_2\text{NH.B}(\text{C}_6\text{F}_5)_4$
 B-3: $\text{Ph}_3\text{C.B}(\text{C}_6\text{F}_5)_4$
 Zr-2: $\text{Ph}_2\text{C}(\text{Cp})(2,7\text{-di-Me-Flu})\text{ZrCl}_2$
 Zr-4: $\text{Et}(\text{inde})_2\text{ZrCl}_2$
 Zr-6: $\text{Me}_2\text{Si}(2,4\text{-Me}_2\text{Cp})_2\text{ZrCl}_2$
 B-2: $\text{C}_7\text{H}_7\text{.B}(\text{C}_6\text{F}_5)_4$

Table 2

Example	Polymer- ization temper- ature (°C)	Metal- locene	Boron com- pound	Aluminum compound	Zr/B/Al (molar ratio)	Zr cata- lyst con- centration (μmol/l)	Ethylene pressure (kg/cm ²)	Comonomer (mol%)	Catalyst solution feed rate (cc/hr)
12	193	Zr-1	B-1	i-Bu ₃ Al	1/2/250	650	950	Hexene-1: 31.4	120
13	180	Zr-1	B-1	i-Bu ₃ Al	1/2/250	650	950	Hexene-1: 28.8	120
14	165	Zr-1	B-1	i-Bu ₃ Al	1/2/250	300	950	Hexene-1: 19.0	70
15	180	Zr-1	B-2	i-Bu ₃ Al	1/2/250	300	950	Hexene-1: 32.6	205
16	165	Zr-1	B-2	i-Bu ₃ Al	1/2/250	300	950	Hexene-1: 33.0	225
17	165	Zr-1	B-1	Et ₃ Al	1/2/250	300	950	Hexene-1: 33.5	315
18	155	Zr-1	B-1	i-Bu ₃ Al	1/1/250	650	1500	Hexene-1: 41.2	45
19	180	Zr-1	B-1	i-Bu ₃ Al	1/1/250	650	900	Butene-1: 39.4	100
20	153	Zr-1	B-1	i-Bu ₃ Al	1/1/250	650	900	Butene-1: 53.9	110
21	150	Zr-3	B-1	i-Bu ₃ Al	1/1/250	300	900	Butene-1: 66.8	305
22	155	Zr-2	B-1	i-Bu ₃ Al	1/2/250	300	900	Hexene-1: 30.0	140
Comparative Example 6	155	Zr-4	B-1	i-Bu ₃ Al	1/2/250	650	950	Hexene-1: 32.0	290

Zr-1: Ph₂C(Cp)(Flu)ZrCl₂
 Zr-3: Ph₂C(Cp)(2,7-di-tBu-Flu)ZrCl₂
 B-1: Ph(Me)₂NH.B(C₆F₅)₄
 Zr-2: Ph₂C(Cp)(2,7-di-Me-Flu)ZrCl₂
 Zr-4: Et(inden)₂ZrCl₂
 B-2: C₇H₇.N(C₆F₅)₄

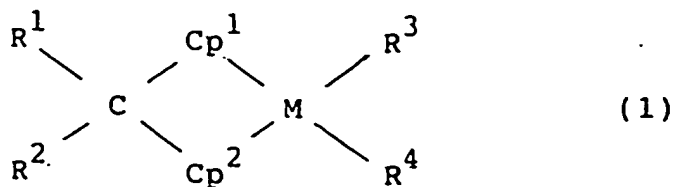
Table 3

Example	Productivity (kg/hr)	Mw ($\times 10^4$)	MWD	MFR (g/10min)	Density (g/cm ³)	Melting point (°C)
12	13.3	5.94	1.8	9.1	0.925	117
13	12.5	6.49	1.7	5.3	0.925	118
14	8.8	7.72	1.8	2.2	0.929	124
15	12.5	6.59	1.8	4.9	0.922	115
16	11.5	7.42	1.9	3.1	0.918	112
17	11.5	7.46	1.8	3.4	0.918	112
18	14.1	6.00	1.7	3.4	0.911	108
19	10.5	4.91	1.6	5.2	0.922	117
20	8.4	5.23	1.7	7.0	0.882	59
21	8.7	5.67	1.9	4.1	0.885	59
22	10.0	7.28	2.0	0.9	0.918	118
Comparative Example 6	26.2	3.72	2.0	70.0	0.932	124

Claims

1. A process for producing an ethylene/ α -olefin copolymer of a weight-average molecular weight of not less than 40000 by copolymerization of ethylene with an α -olefin having three or more carbons by use of an olefin polymerization catalyst at a polymerization temperature of not lower than 120 °C: the olefin polymerization catalyst comprising, as constitutional components, a) a metallocene compound, b) an ionizing ionic compound, and c) an organoaluminum compound:
the metallocene compound (a) being a compound represented by the general formula (1):

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wherein Cp^1 and Cp^2 are independently a substituted or unsubstituted cyclopentadienyl, indenyl, or fluorenyl group; R^1 and R^2 are independently a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkoxy group, a substituted or unsubstituted aryl group, or a hydrogen atom; M is titanium or zirconium; R^3 and R^4 are independently a hydrogen atom, a halogen atom, a hydrocarbon group of 1 to 12 carbons, an alkoxy group, or an aryloxy group, the ionizing ionic compound (b) being a compound which is capable of changing the metallocene compound (a) into a cationic form and does not further react with the cationic form of the metallocene compound, and the organoaluminum compound (c) being represented by the general formula (2):

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wherein R^5 , $R^{5'}$, and $R^{5''}$ are independently a hydrogen atom, a halogen atom, an amino group, an alkyl group, an alkoxy group, or an aryl group, at least one thereof being an alkyl group.

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2. The process for producing an ethylene/ α -olefin copolymer according to claim 1, wherein the substituent Cp^2 of the metallocene compound is a substituted or unsubstituted fluorenyl group.
3. The process for producing an ethylene/ α -olefin copolymer according to claim 1, wherein at least one of the substituents R^1 and R^2 of the metallocene compound is a substituted or unsubstituted aryl group.
4. The process for producing ethylene/ α -olefin copolymer according to claim 1, wherein the substituent Cp^2 is a substituted or unsubstituted fluorenyl group and at least one of the substituents R^1 and R^2 is a substituted or unsubstituted aryl group in the metallocene compound.

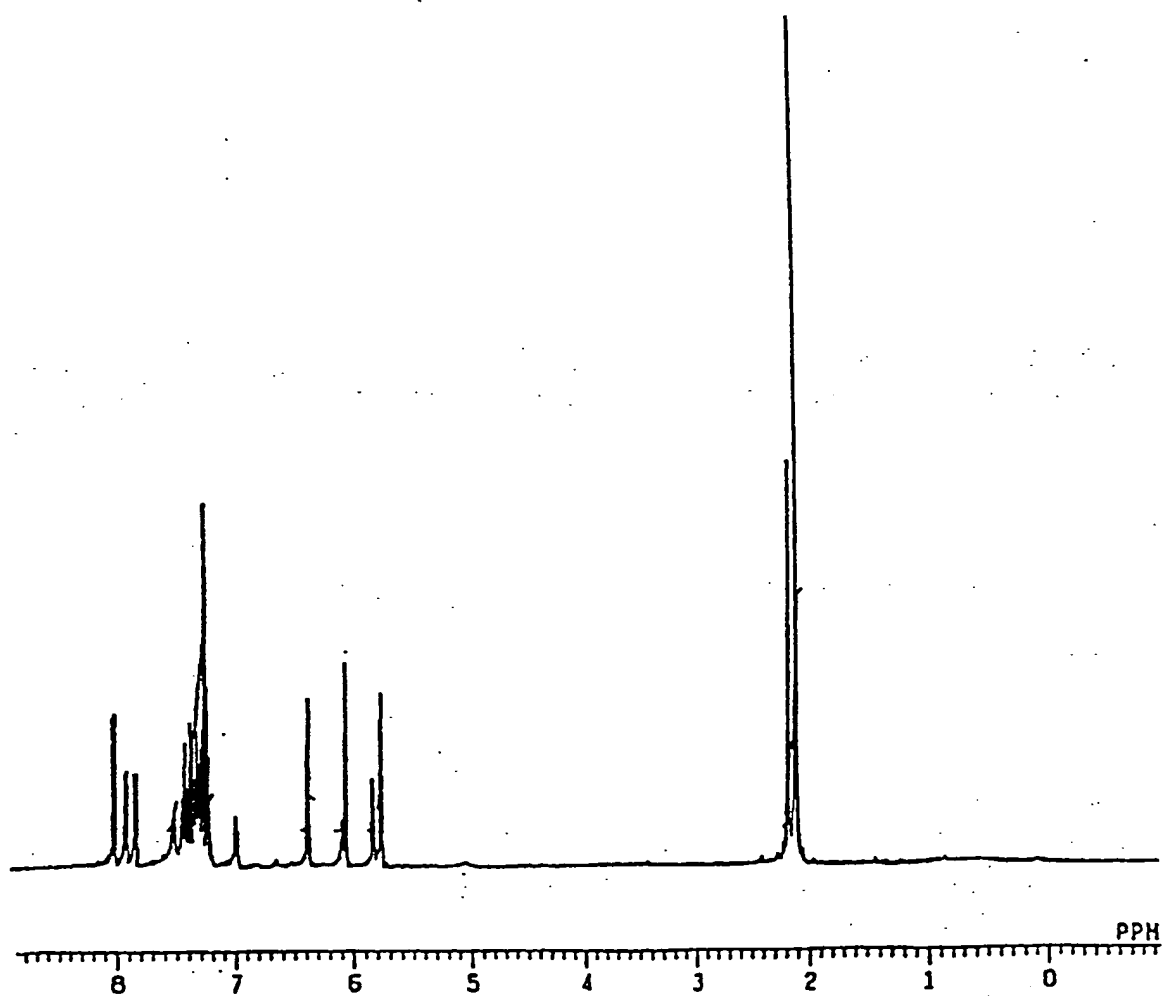
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FIG. 1





European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 94 10 2579

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL.5)
A	EP-A-0 426 638 (FINA TECHNOLOGY, INC) * example 33 *	1	C08F210/16
D	& JP-A-3 207 704 (...) ---		
A	DIE MAKROMOLEKULARE CHEMIE RAPID COMMUNICATIONS vol. 14, no. 2, February 1993 pages 109 - 114 XP334497 CHIEN JAMES 'Olefin copolymerization and olefin/diene terpolymerization with a zirconium catalyst system' ---	1	
A	EP-A-0 513 380 (IDEMITSU KOSAN COMPANY) * claims 1,5 * * page 10, line 24 - line 25 * * page 10, line 47 * * example 22 * -----	1-4	
			TECHNICAL FIELDS SEARCHED (Int. CL.5)
			C08F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 26 May 1994	Examiner Fischer, B
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	